Microscopy Investigation on the Fading Mechanism of Electrode Materials

Chong-Min Wang

Pacific Northwest National Laboratory

2016 DOE Vehicle Technologies Program Review
June 06-10, 2016

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Pacific Northwest
NATIONAL LABORATORY

Project ID#: ES226

Overview

Timeline

- Start date: Oct. 1, 2015
- End date: Sept. 30, 2018
- Percent complete:25%

Budget

- Total project funding: $900k
  - DOE share: 100%
- Funding for FY16: $300k

Barriers addressed

- Fading and failure mechanism of electrodes
- High theoretical capacity of electrode materials cannot be fully utilized

Partners

- Material synthesis group in PNNL
- Lawrence Berkeley National Lab
- Argonne National Lab
- Stanford University
- National Renewable Energy Lab
- GM Research Center
- Sandia National Laboratory
- University of Texas at Austin
- Hydro Quebec
- EnerG2 company
- FEI Company
- Hummingbird Scientific Inc.

Relevance/Objectives

- Develop *ex-situ*, *in situ* and *operando* HRTEM and associated spectroscopic techniques for rechargeable battery research

- Use *ex-situ*, *in situ* and *operando* HRTEM and in-situ spectroscopic technique to probe the fading mechanism of electrode materials

- Correlation of structural and chemical evolution with battery performance for guiding the designing of new materials

Milestones

- Using multi-scale quantitative atomic level mapping to identify the behavior of Co, Ni, and Mn in NCM during battery charge/discharge (03/31/2016). Complete

- Complete quantitative measurement of structural/ chemical evolution of modified-composition NCM cathode during cycling of battery (06/31/2016). On track

- Identify the correlation between the structure stability and charge voltage of NCM for optimized charge voltage (9/30/2016). On track

Pacific Northwest
NATIONAL LABORATORY

Approach/Strategy

- Using the state-of-the-art aberration corrected S/TEM, EELS, and EDS to probe chemistry and structure of electrode

- Extend and enhance the unique ex-situ and in situ S/TEM methods and associated spectroscopic technique for probing the fading mechanism of Li-ion battery under dynamic operating condition

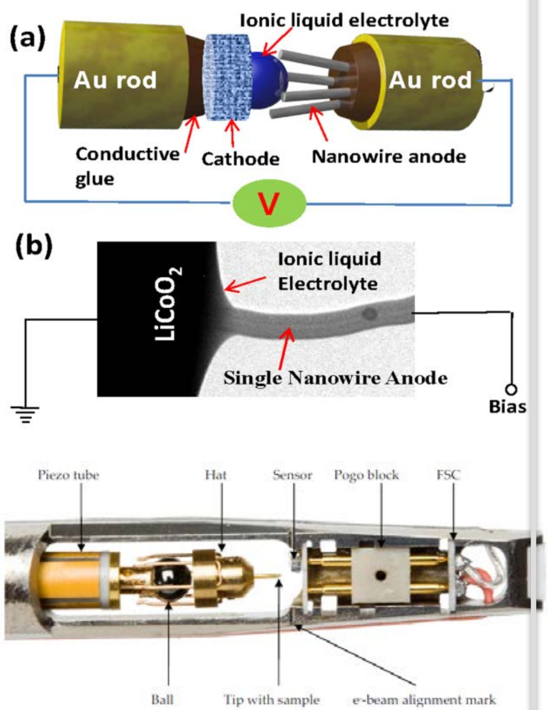
- Establish close collaboration/integration with battery research and development groups to capture the cutting edge questions that facing the battery research/ development

Pacific Northwest
NATIONAL LABORATORY

Technical Accomplishments:

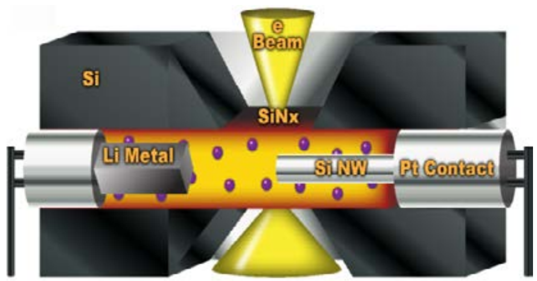
Developed In-Situ Liquid SIMS to Probe SEI Layer Chemistry in Lithium Ion Battery: Complimentary with In-Situ TEM Results

Open cell in-situ TEM



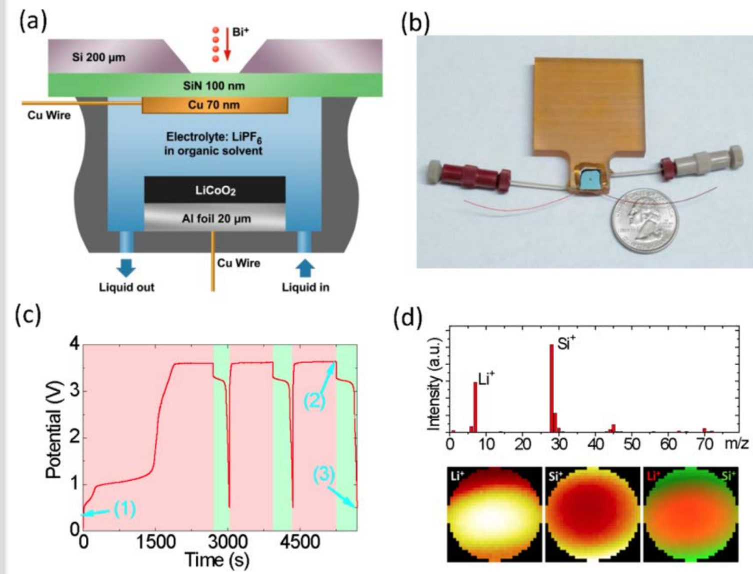
J. Y. Huang and C. M,. Wang et al, Science, 330(2010)1515

Closed cell in-situ TEM



M. Gu and C. M. Wang et al, Nano Letter, 13 (2013)6106

In-Situ liquid SIMS



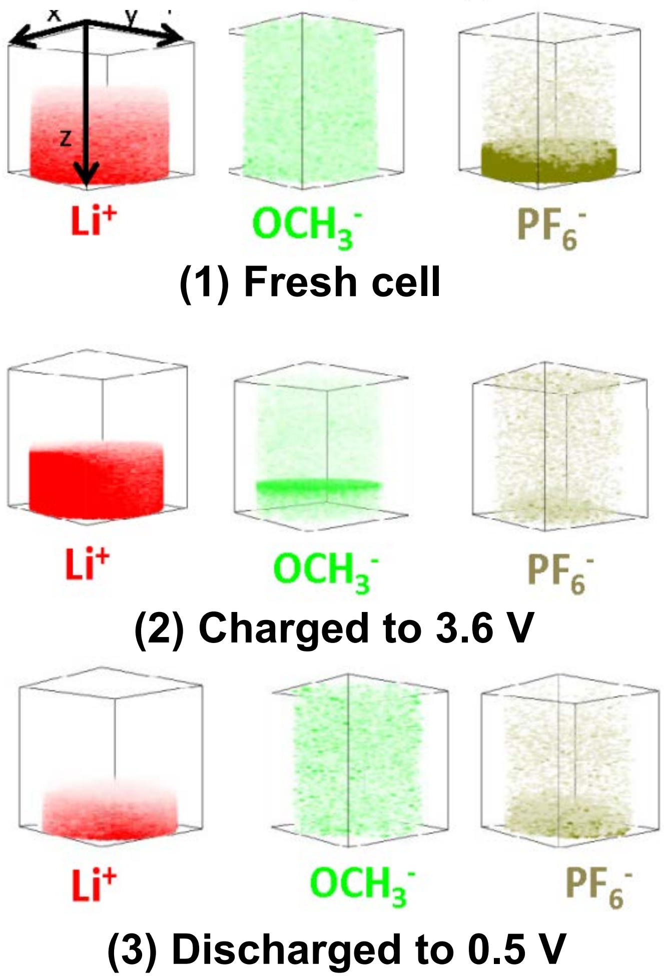
Z. H. Zhu and C. M. Wang et al, Nano Letter, 15 (2015)6170

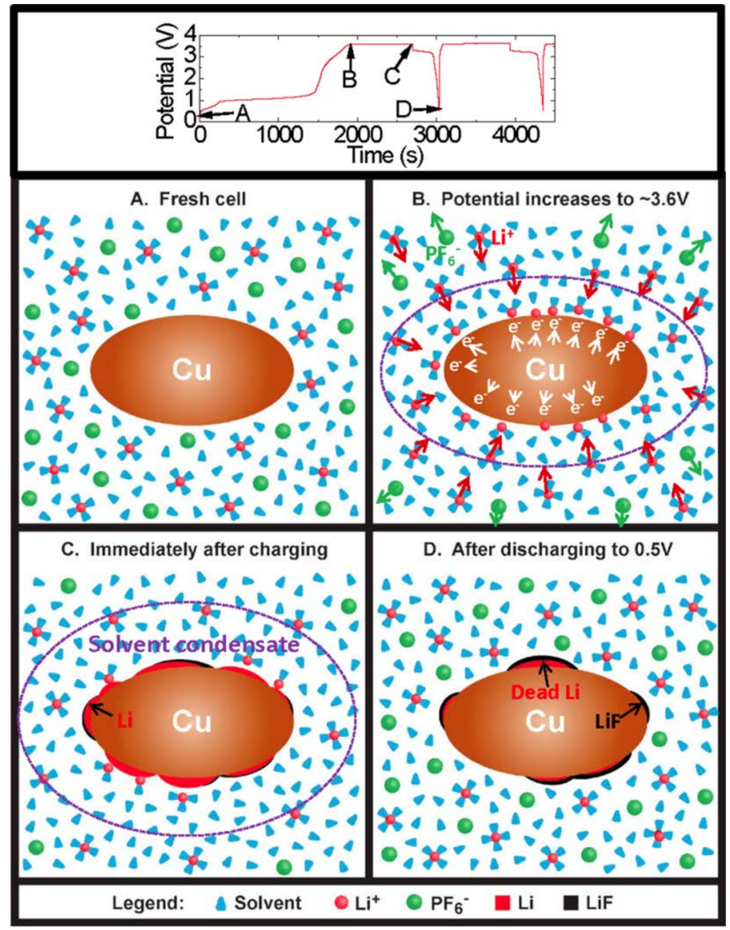
Towards real battery operating condition

Pacific Northwest NATIONAL LABORATORY

Technical Accomplishments:

In-situ Liquid SIMS Probing of Electrode Surface Chemical Evolution during the Charge and Discharge of the Lithium Ion Battery





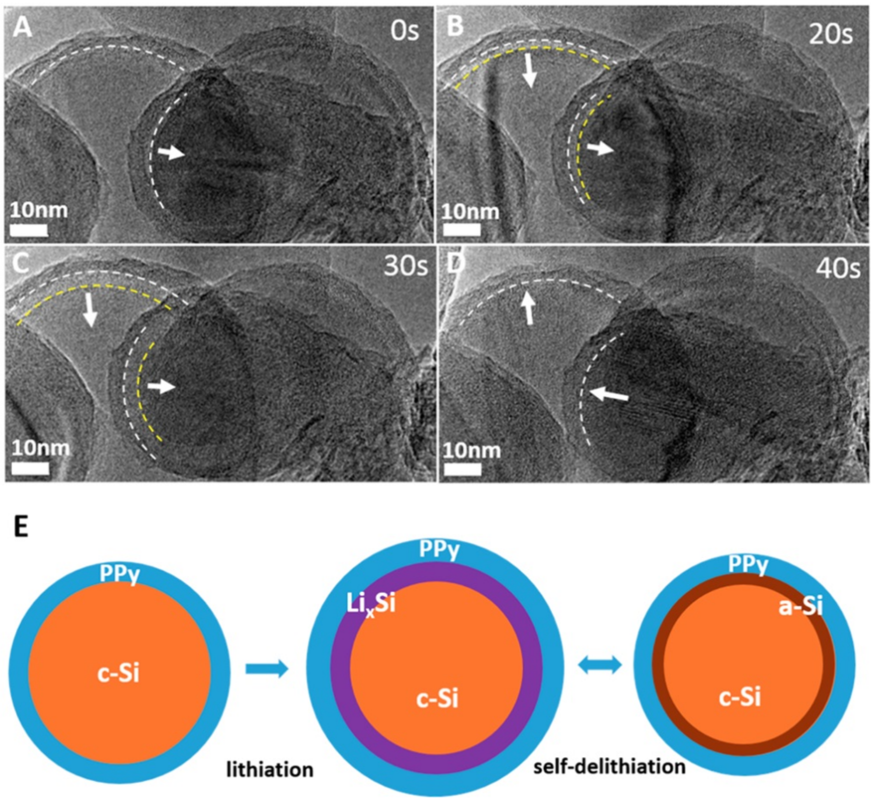
- Direct observation of the polarization of the ions during the charge and discharge cycle

Pacific Northwest NATIONAL LABORATORY

Z. H. Zhu and C. M. Wang et al, Nano Letter, 15 (2015)6170

Technical Accomplishments:

A Strong Confinement of Surface Coating Layer Leads to Self Discharging of the Battery



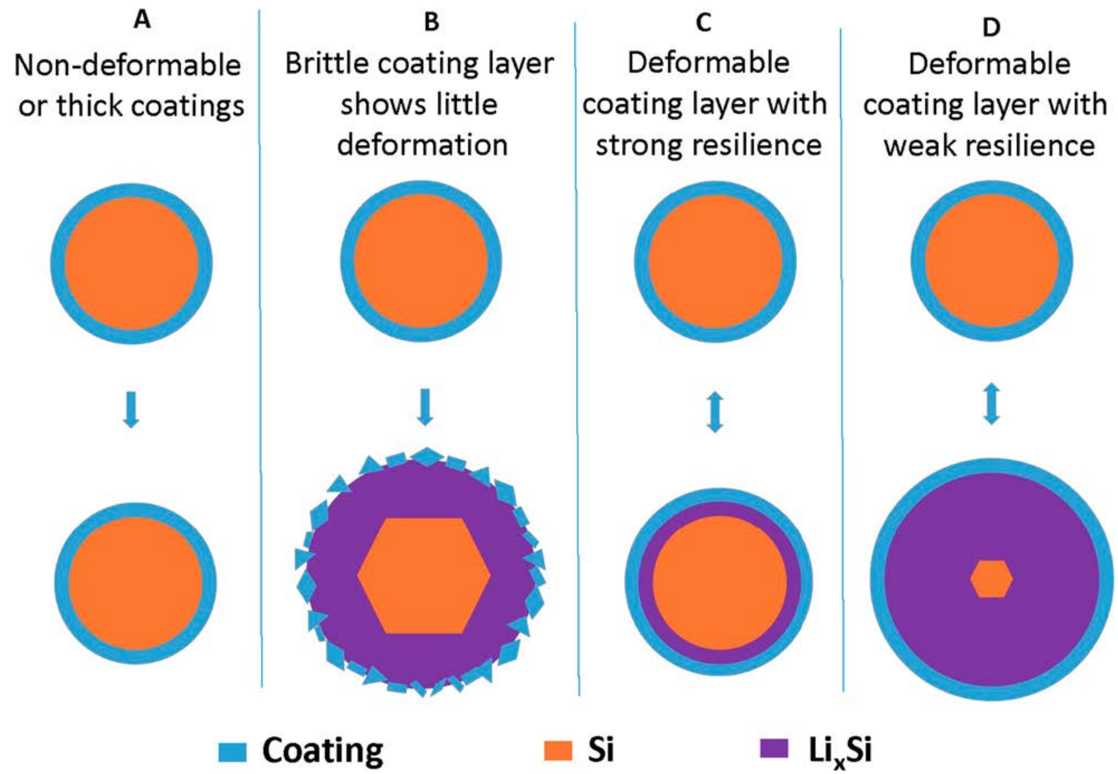
- Time-resolved in-situ TEM images depict the "fluctuation" of two SiNPs coated with polypyrrole during lithiation process
- The white dash lines in A-D indicate the interface between c-SiNP and PPy coating, and yellow dash lines in B,C indicate the interface between c-Si core and a-LixSi shell
- The white arrows show the moving directions of the interface
- E is the schematic of three stages during "fluctuation" lithiation of a coated SiNP

▶ This in-situ TEM observation reveals that a strong surface coating may lead to self-discharging of the battery

Langli Luo and C. M. Wang et al, Nano Letter. 15 (2015) 7016

Pacific Northwest NATIONAL LABORATORY

Technical Accomplishments:
Selection Principle of Coating Layer Characteristics for Optimized Designing of Battery Performance



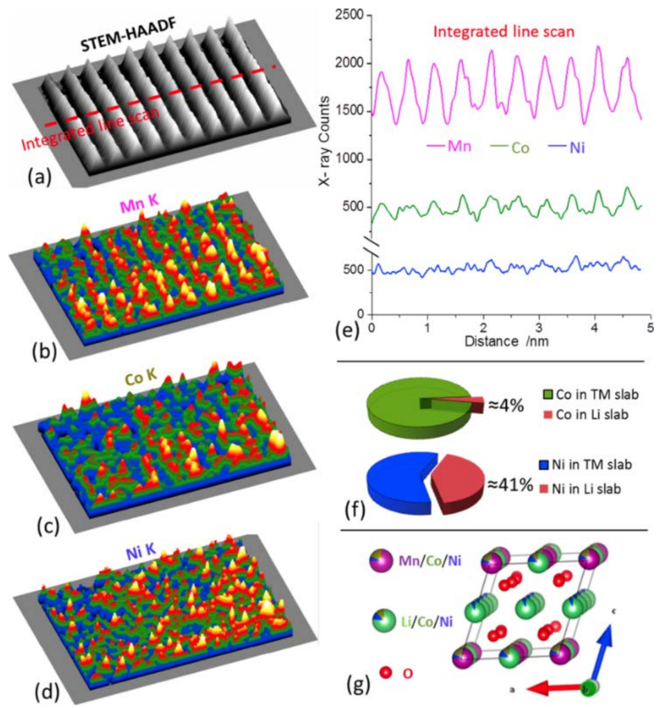
Schematic drawings to illustrate the effect of surface coatings on lithiation behavior.

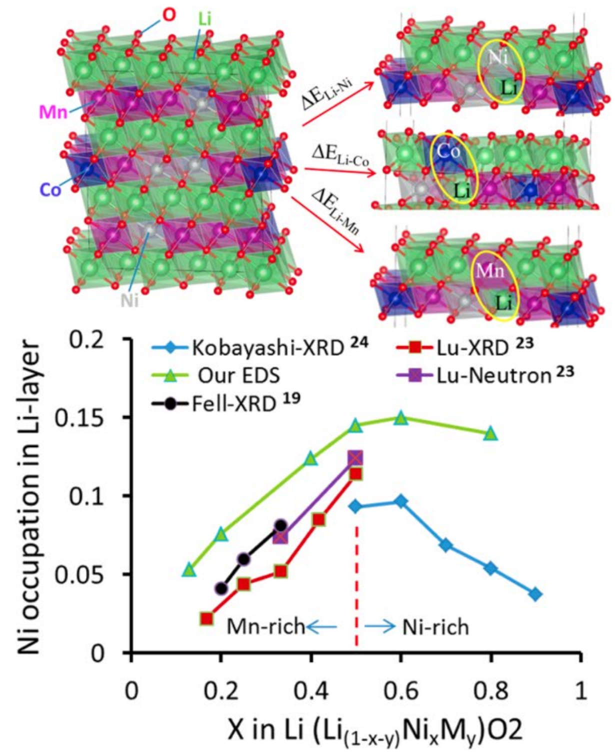
- (A) Extremely hard or thick coatings lead to no lithiation.
- (B) Brittle coating leads to break of the surface coating during the lithiation.
- (C) Deformable coating with strong resilience will lead to alternation of lithiation kinetics.
- (D) Deformable coating with weak resilience will have weak retardation to lithiation.

Langli Luo and C. M. Wang et al, Nano Letter. 15 (2015) 7016

Technical Accomplishments:

How does Co, Ni, and Mn Mix with Li Layer: Essential for Addressing the Voltage Fading; Elemental Distribution in $Li_{1.2}Ni_{0.13}Co_{0.17}Mn_{0.5}O_2$ (NC-LMR)





Comparison: EDS; XRD; Neutron diffraction; coupling with theoretical calculations

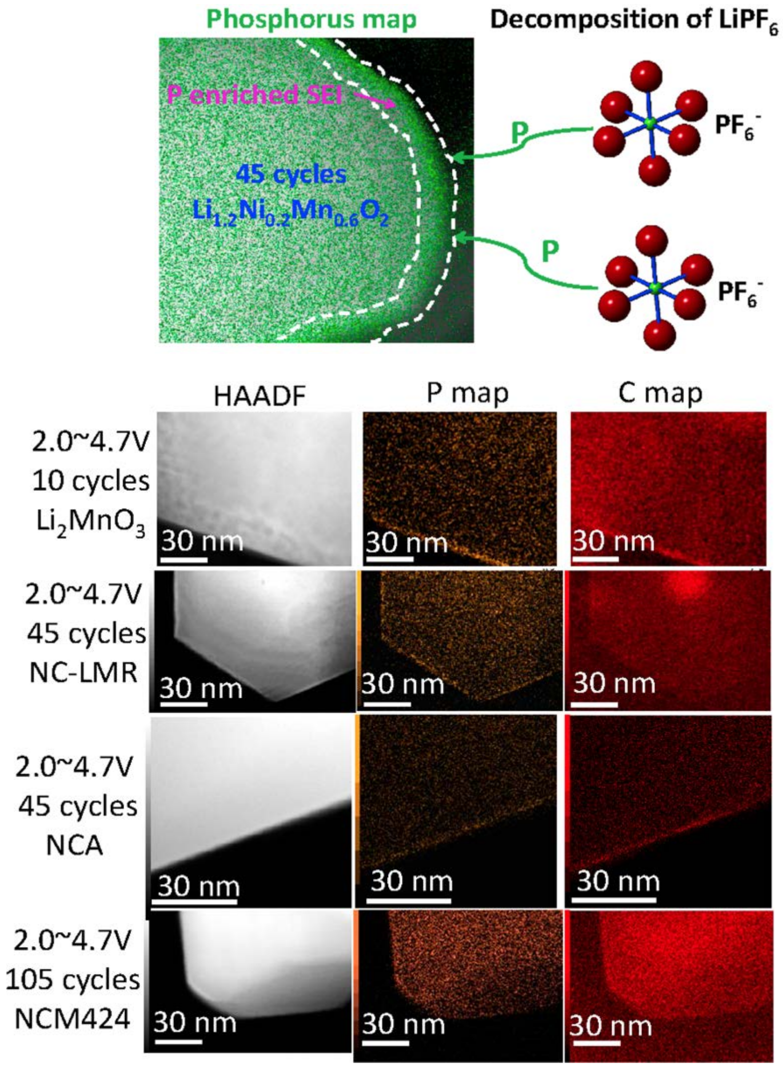
- In $Li_{1.2}Ni_{0.13}Co_{0.17}Mn_{0.5}O_2$ (NC-LMR), Ni is prone to reside at the Li layer than Co and Mn. 41% Ni and 4% Co were estimated to seat in Li-layer

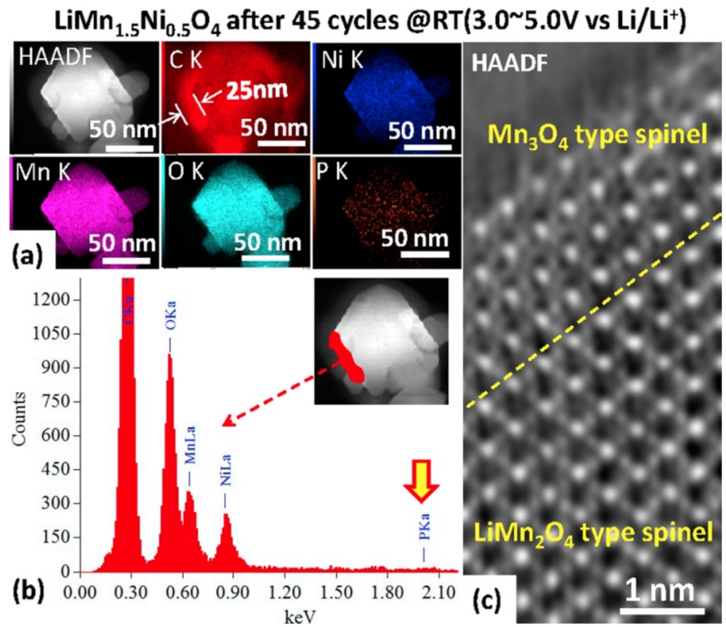
Pacific Northwest NATIONAL LABORATORY

Pengfei Yan et al, Chem. Mater., 27, 5393-5401(2015)

Technical Accomplishments:

Phosphorous Enrichment in SEI Layer on Cathode Indicates Cathode-Electrolyte ($LiPF_6$ in EC-DMC) Interaction Leads to Electrolyte Depletion of Salt





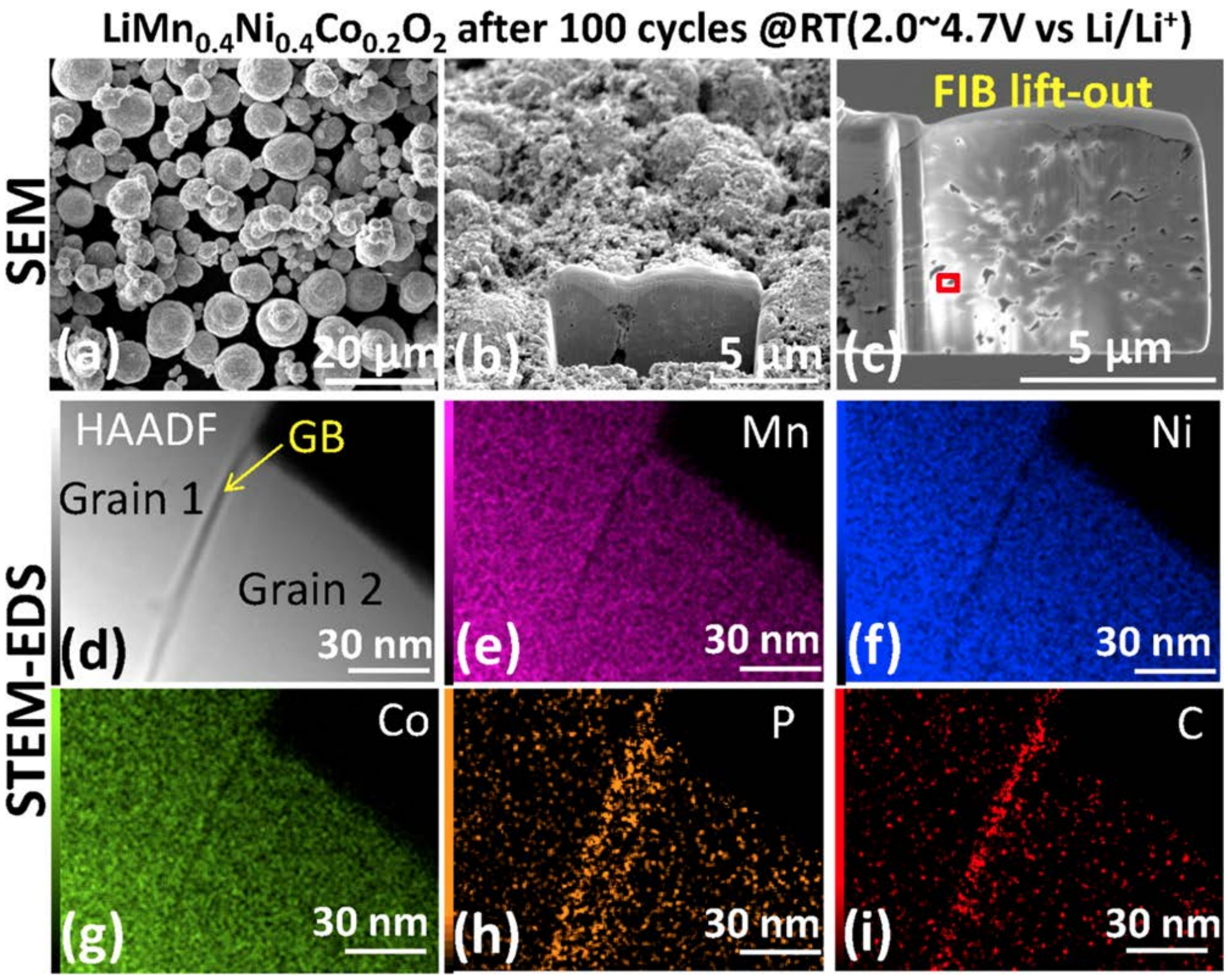
- Structure, voltage, and temperature affect the electrolyte decomposition.
- Spinel phase is more stable than layered structure

Pacific Northwest NATIONAL LABORATORY

Pengfei Yan et al, Chem. Mater., 27, 7447-7451(2015)

Technical Accomplishments:

Phosphorous Enrichment on the Particle Boundaries in the Large Aggregates of NMC Particles



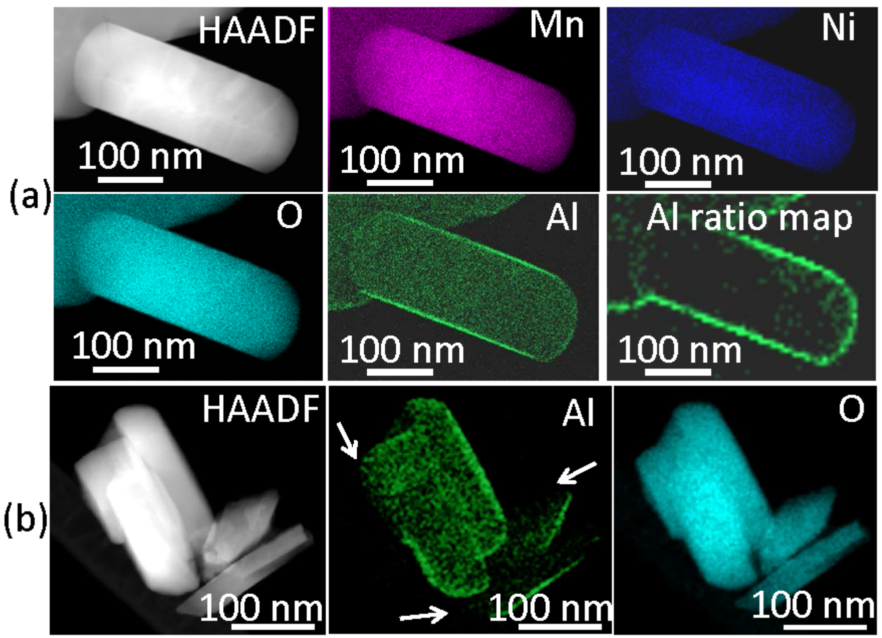
- The liquid electrolyte penetrate into the boundaries formed by the particle aggregates

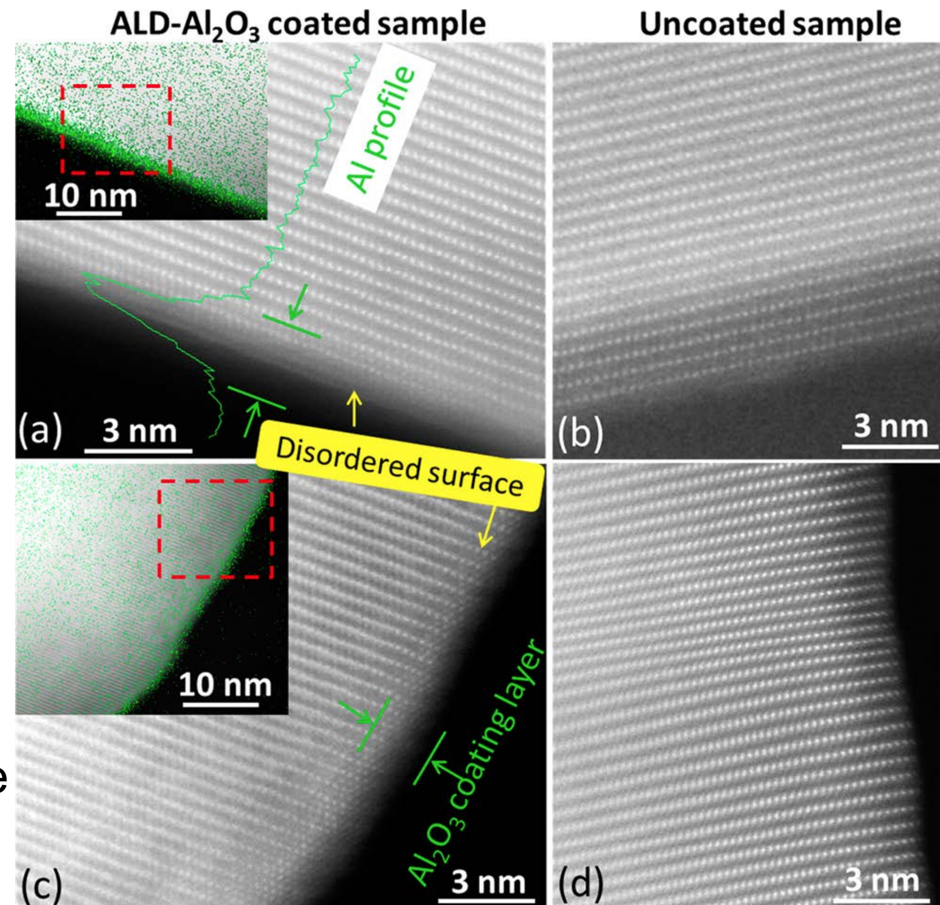
Pengfei Yan et al, Chem. Mater., 27, 7447-7451(2015)

Pacific Northwest NATIONAL LABORATORY

Technical Accomplishments:

Mitigation of Cathode-Electrolyte Reaction by Surface Coating: Chemical and Structural Information of $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ Coated with Al_2O_3 Using ALD





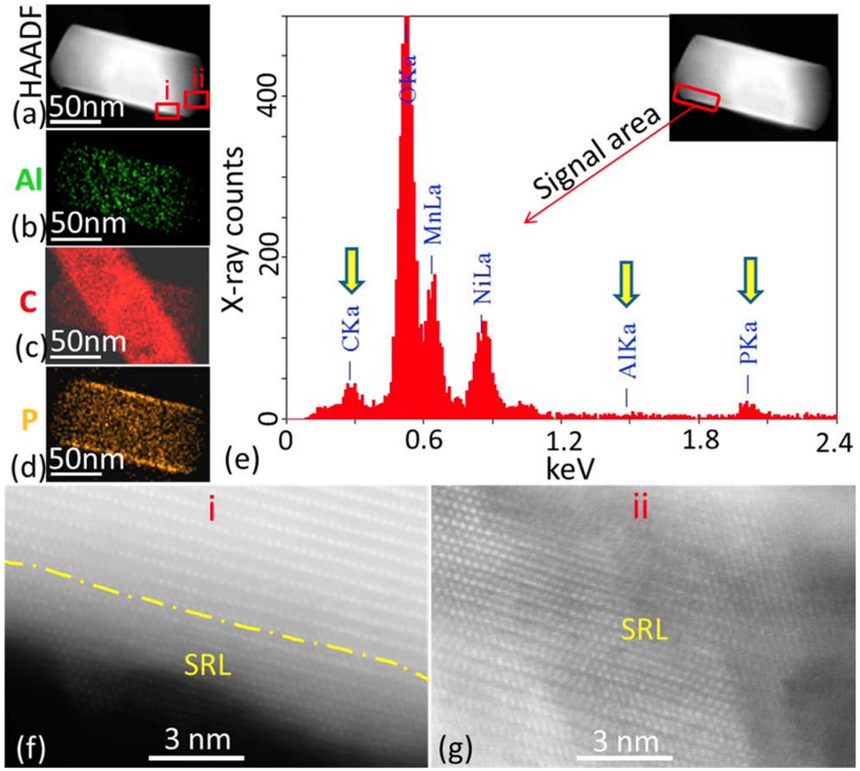
- ALD generally gives uniform coating layer on the particle surface as revealed by the STEM-EDS mapping
- Coating leads to structural modification of the particle surface

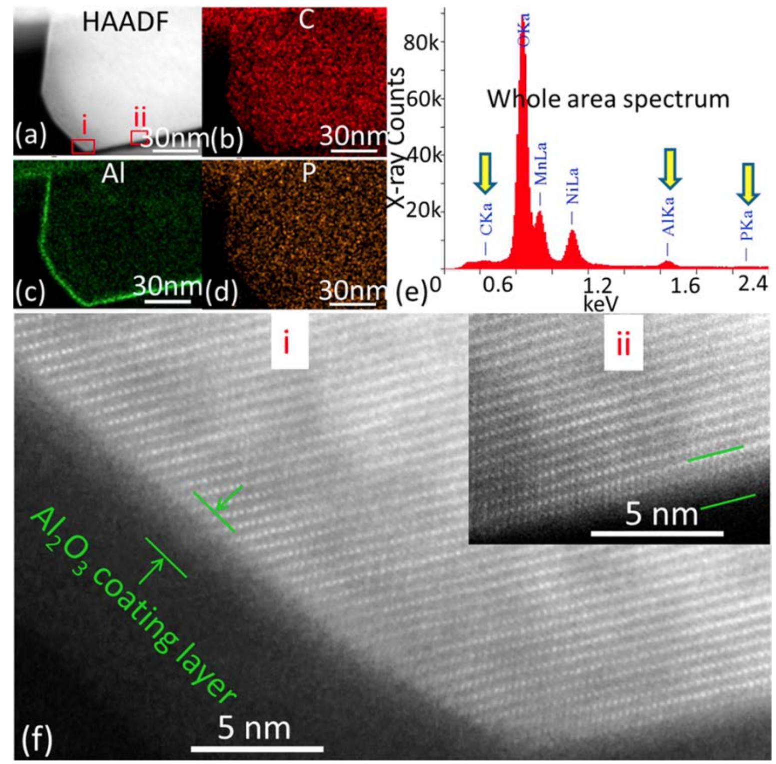
Pacific Northwest NATIONAL LABORATORY

Pengfei Yan et al, Chem. Mater., 28, 857(2016)

Technical Accomplishments:

Direct Visualization of How Al_2O_3 Coating Affects the Surface Chemistry and Structure of $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$



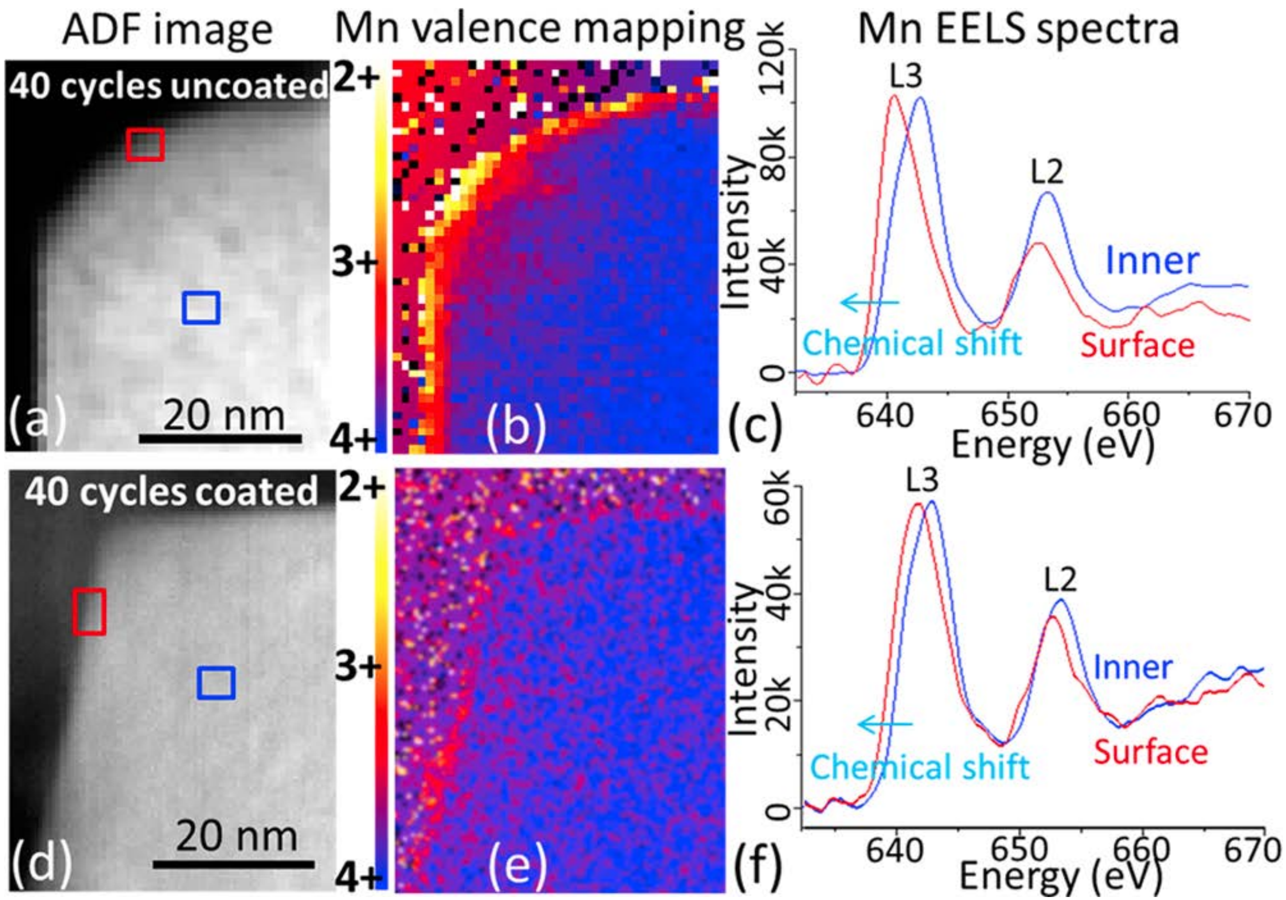


Al_2O_3 coating effect:

- Suppress cathode-electrolyte reaction
- Mitigate the surface Mn reduction and dissolution
- Suppress layer to spinel phase transition

Pengfei Yan et al, Chem. Mater., 28, 857(2016)

Technical Accomplishments:
Direct Visualization of How Al_2O_3 Coating Affects the Surface Electronic Structure of $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$



- Use STEM−EELS to map valence of LMR cathode after 40 cycles and study the effect of the Al_2O_3 coating layer
- With the Al_2O_3 coating, the reduction of Mn is mitigated at the particle surface

Pengfei Yan et al, Chem. Mater., 28, 857(2016)

Pacific Northwest NATIONAL LABORATORY

Responses to Previous Year Reviewers' Comments

- **The reviewers comments are very positive:**

... The in-situ and in-Operando tools developed by the PIs are especially important to the field…

…the materials and issues they selected are all of high-importance to the DOE BMR programs.

… this work is a big step forward in characterization of battery electrode materials…

….PI's work on Si anodes and other cathodes is excellent

Comment: Electron beam effect during imaging
Response: Electron beam may indeed affect the sample, this can be calibrated and mitigated by controlling the electron dose. A paper has been published to address this

Comment: Use closed cell to study SEI layer and the best resolution that can be reached
Response: The best resolution can be reached is in the nanometer scale. Focused effort on closed liquid cell now for improving the resolution

Comment: To focus more on high energy electrode study
Response: Totally agree with reviewer and we are focusing on that direction

Collaboration and Coordination with Other Institutions

Partners:

- Material synthesis group in PNNL: Preparation of both cathode and Si based anode materials
- Argonne National Lab: Preparation of cathode materials, ALD coating
- Lawrence Berkeley National Lab: Preparation of cathode materials
- Stanford University: Si nanowire based anode and surface coating
- GM Research Center: Prepared porous Si, S enclosed in carbon
- National Renewable Energy Lab: ALD coated Si samples
- Sandia National Laboratory: STEM EDS observation
- Hummingbird Scientific: Help to develop the liquid holder
- University of Texas at Austin: Preparation of cathode and anode materials
- FEI Company: EDS capability development

Pacific Northwest NATIONAL LABORATORY

Remaining Challenges and Barriers

- A primary challenge for in-situ and operando TEM study of battery is the loading of Li metal anode into the liquid cell. Addressing this problem will rely on new design of chips for liquid cell

- TEM and STEM imaging resolution needs to be optimized by minimizing the liquid layer thickness. This can be achieved by designing of the liquid window geometry to minimize the bulging effect

- Due to the complicated steps of assembling the in-situ cell, the reliability and reproducibility of the in-situ and operando TEM cell need to be improved

Pacific Northwest
NATIONAL LABORATORY

Proposed Future Work

❖ **FY2016**

- Complete the in-situ TEM study of the lithiation behavior of Si-SiO_x composite
- Continue the study of the surface segregation behavior of Co, Ni, and Mn in LMR, NCM, and NCA based cathode and correlate with fading mechanism
- In-situ TEM study of the Ni, Co and Mn surface segregation and its correlation with the materials fabrication temperature

❖ **FY2017**

- Using various microscopic and spectroscopic techniques, including open-cell, in-situ and *operando* TEM and in-situ liquid SIMS system to diagnose the structural and chemical evolution of electrode materials upon cycling of the battery
- Investigate the fading mechanism of Si based anode materials, focusing on Si-C composite system
- Investigate the voltage and capacity fading in cathodes, focusing on NMC and NCA system

Summary

- Developed in-situ liquid SIMS that enables the direct probing of the molecular structure and chemistry of SEI layer for lithium ion battery

- In-situ TEM observation reveals that the coating layer characteristics on Si affects the lithiation behavior of the Si, leading to a potential of guided selection and designing of coating layer.

- Observed new chemistry of SEI layer in cathode material, direct visualizing the P enrichment on the cathode particle surface, indicating the cathode-electrolyte side reaction and this reaction depends on: voltage, temperature, and crystal surface structure

- Atomic level quantification of Ni, Co, and Mn mixing with Li layer, discovered that Ni shows high propensity of mixing with Li than Co and Mn in the layer structured cathode

- Clarified the role of surface coating on cathode for enhanced battery performance: prevent surface structural phase transition; mitigate the side reaction with electrolyte; reduce the Mn reduction and dissolution

Pacific Northwest
NATIONAL LABORATORY

Technical Back-Up Slides

Pacific Northwest
NATIONAL LABORATORY

Patents/Publications/Presentations

1. Yan, P. F.; Zheng, J. M.; Lv, D. P.; Wei, Y.; Zheng, J. X.; Wang, Z. G.; Kuppan, S.; Yu, J. G.; Luo, L. L.; Edwards, D.; Olszta, M.; Amine, K.; Liu, J.; Xiao, J.; Pan, F.; Chen, G. Y.; Zhang, J. G.; Wang, C. M. Atomic-Resolution Visualization of Distinctive Chemical Mixing Behavior of Ni, Co, and Mn with Li in Layered Lithium Transition-Metal Oxide Cathode Materials. *Chemistry of Materials* 2015, 27, 5393-5401.

2. Yan, P. F.; Xiao, L.; Zheng, J. M.; Zhou, Y. G.; He, Y.; Zu, X. T.; Mao, S. X.; Xiao, J.; Gao, F.; Zhang, J. G.; Wang, C. M. Probing the Degradation Mechanism of Li2MnO3 Cathode for Li-Ion Batteries. *Chemistry of Materials* 2015, 27, 975-982.

3. Yan, P.; Nie, A.; Zheng, J.; Zhou, Y.; Lu, D.; Zhang, X.; Xu, R.; Belharouak, I.; Zu, X.; Xiao, J.; Amine, K.; Liu, J.; Gao, F.; Shahbazian-Yassar, R.; Zhang, J.-G.; Wang, C.-M. Evolution of Lattice Structure and Chemical Composition of the Surface Reconstruction Layer in Li1.2Ni0.2Mn0.6O2 Cathode Material for Lithium Ion Batteries. *Nano Lett.* 2015, 15, 514-522.

4. Xiao, Q.; Gu, M.; Yang, H.; Li, B.; Zhang, C.; Liu, Y.; Liu, F.; Dai, F.; Yang, L.; Liu, Z.; Xiao, X.; Liu, G.; Zhao, P.; Zhang, S.; Wang, C.; Lu, Y.; Cai, M. Inward lithium-ion breathing of hierarchically porous silicon anodes. *Nature Comm.* 2015, 6, 8844.

5. Luo, L. L.; Zhao, P.; Yang, H.; Liu, B. R.; Zhang, J. G.; Cui, Y.; Yu, G. H.; Zhang, S. L.; Wang, C. M. Surface Coating Constraint Induced Self-Discharging of Silicon Nanoparticles as Anodes for Lithium Ion Batteries. *Nano Letters* 2015, 15, 7016-7022.

6. Luo, L. L.; Yang, H.; Yan, P. F.; Travis, J. J.; Lee, Y.; Liu, N.; Piper, D. M.; Lee, S. H.; Zhao, P.; George, S. M.; Zhang, J. G.; Cui, Y.; Zhang, S. L.; Ban, C. M.; Wang, C. M. Surface-Coating Regulated Lithiation Kinetics and Degradation in Silicon Nanowires for Lithium Ion Battery. *ACS Nano* 2015, 9, 5559-5566.

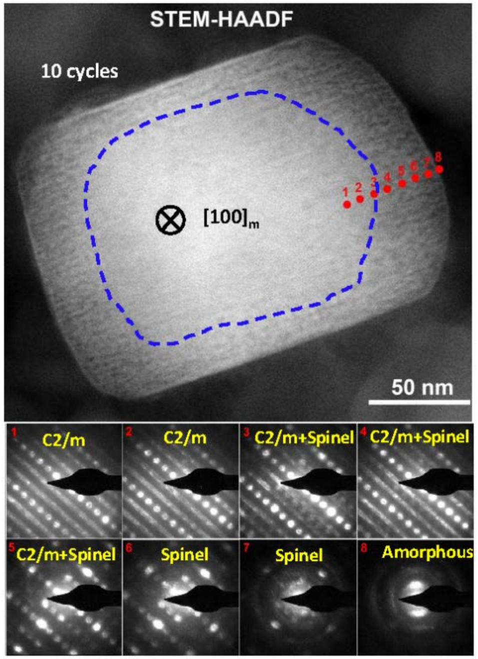
Pacific Northwest
NATIONAL LABORATORY

Acknowledgements

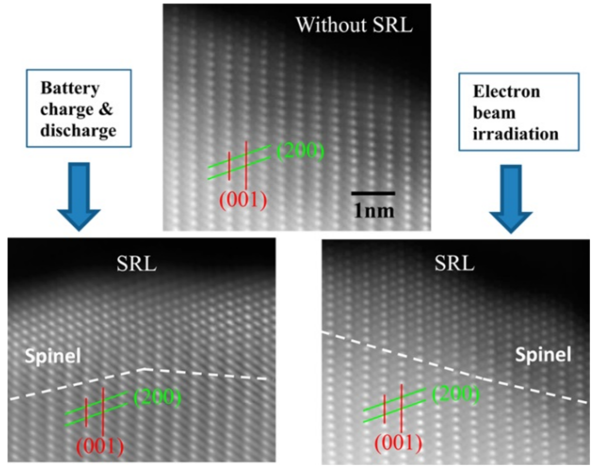
- ✓ Supports from the U.S. Department of Energy, Office of Vehicle Technologies Program are gratefully appreciated.

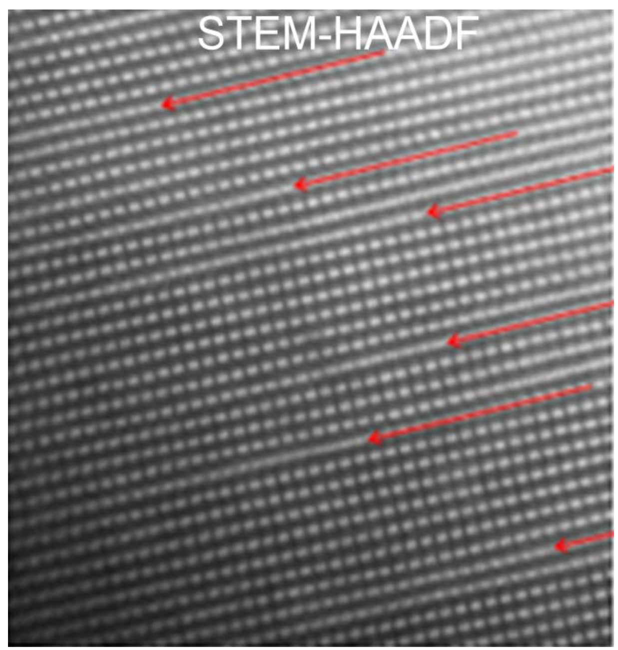
- ✓ Team Members:
  Pengfei Yan, Langli Luo, Jianming Zheng, Meng Gu, Wu Xu, Xiaolin Li, Jie Xiao, Jun Liu, and Ji-Guang Zhang

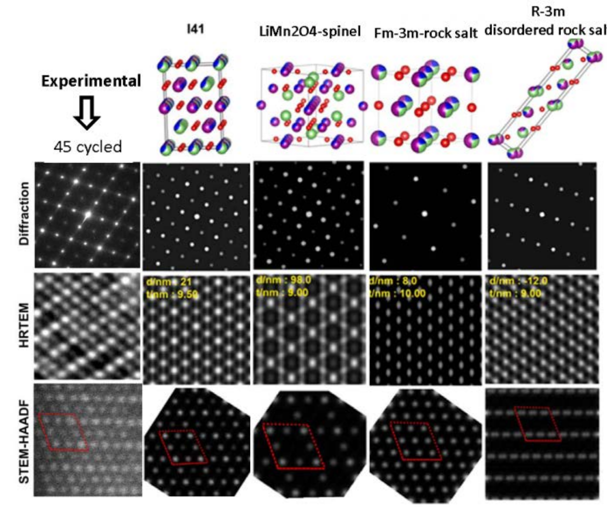
The Structure Change Route of Li_2MnO_3 Synthesized by CP Method



8-position line scan of a 10-cycles sample using nano beam electron diffraction. The crystal orientation can be assigned to [100] for C2/m structure and [112] for spinel structure.







Comparison between experimental results and simulation results of different crystal models for the SRL from the [010] zone axis. I41 structure matches best in the four crystal models.

Pacific Northwest
NATIONAL LABORATORY